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# Direct Observation of Orbital Ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ Using Soft X-ray Diffraction

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We report the first direct resonant soft x-ray scattering observations of orbital ordering. We have studied the low temperature phase of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , a compound that displays charge and orbital ordering. Previous claims of orbital ordering in such materials have relied on observations at the manganese  $K$  edge. These claims have been questioned in several theoretical studies. Instead we have employed resonant soft x-ray scattering at the manganese  $L_{\text{III}}$  and  $L_{\text{II}}$  edges which probes the orbital ordering directly. Energy scans at constant wave vector are compared to theoretical predictions and suggest that at all temperatures there are two separate contributions to the scattering: direct orbital ordering and strong cooperative Jahn-Teller distortions of the  $\text{Mn}^{3+}$  ions.

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Nearly 50 years ago, Goodenough [1] proposed that perovskite manganites such as  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  would be orbitally ordered, consisting of a low temperature insulating phase containing two sublattices resulting from charge ordering between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. In addition, this would be accompanied by orbital ordering, whereby the  $3d_{3z^2-r^2}$   $\text{Mn}^{3+}$  orbitals (associated with the long  $\text{Mn}^{3+}$ -O bonds in the Jahn-Teller distorted  $\text{Mn}^{3+}\text{O}_6$  octahedra) in the form of zigzag chains. This ordering would entail concomitant displacements of the  $\text{Mn}^{4+}\text{O}_6$  octahedra. Since then various crystallographic studies have established the correlation between structural, magnetic, and transport properties, and have detailed the charge and spin ordering observed at low temperatures in addition to the correlated Jahn-Teller distortions. Until recently, however, very little was known about the role of orbital ordering. This situation has changed dramatically in the past few years following the claim of direct detection of orbital ordering by resonant x-ray scattering techniques. Murakami *et al.* [2] employed anomalous scattering to observe orbital ordering in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ . By tuning to the  $\text{Mn}^{3+}$   $K$  edge, they observed a sharp reflection at  $(\frac{3}{4}, \frac{3}{4}, 0)$ . The observation of such reflections is ruled out by the crystal symmetry of the high temperature structure, and can proceed only if the symmetry is reduced by some mechanism, such as the Jahn-Teller effect. Such resonant techniques have since been used to claim orbital order in a number of manganites such as  $\text{LaMnO}_3$  [3] and other materials, based on the assumption that anisotropy in the Mn  $4p$  band, probed by  $1s$ - $4p$  excitations at the Mn  $K$  edge, arises from interaction with the anisotropic  $3d$  states. The claim that such

techniques offer a direct probe of orbital ordering has attracted considerable criticism and debate [4–7]. Theoretical studies have shown that a more likely explanation is that the isotropic resonance effect is caused by the oxygen displacements related to the cooperative Jahn-Teller effect. Recently, a theoretical paper suggested the use of resonant x-ray scattering at the  $L_{\text{III}}$  and  $L_{\text{II}}$  edges of  $\text{Mn}^{3+}$  [8], which directly probe the  $3d$  states and give energy resonances which distinguish between the two.

In a previous paper [9], we demonstrated how it was possible to use resonant enhancement at the  $L$  edge of manganese to observe antiferromagnetic ordering at low temperatures. In this Letter, we report the first unambiguous observation of orbital ordering using soft x-ray diffraction and will demonstrate by using the specific theoretical predictions of Castleton and Altarelli [8] that the orbital ordering is caused by Jahn-Teller displacements.

$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  is a typical transition metal oxide displaying strongly correlated electron states. Upon cooling, the material undergoes a phase transition at  $T_{\text{CO}} = 240$  K into a charge ordered state in which there is a unit difference in the valence states between subsequent manganese atoms (see Fig. 1). In addition to the structural Bragg reflections of the high temperature  $I4/mmm$  phase ( $a = b = 3.86$  Å,  $c = 12.40$  Å), other reflections at a wave vector of  $(\frac{1}{2}, \frac{1}{2}, 0)$  have been observed which are a result of this charge ordered state that doubles the unit cell [10]. In addition, peaks with a wave vector of  $(\frac{1}{4}, \frac{1}{4}, 0)$  have been observed in electron diffraction measurements [11,12]. However, subsequent x-ray and neutron studies have confirmed the presence of the quarter-wave

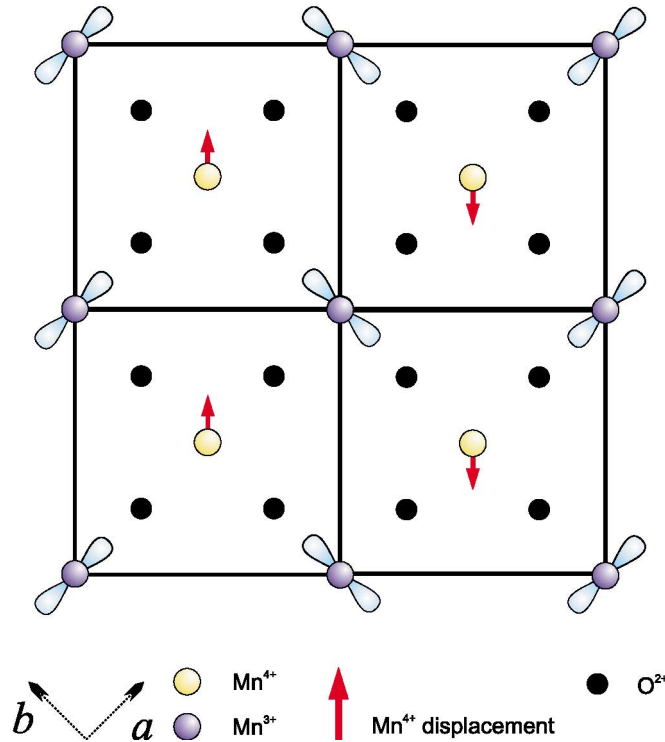


FIG. 1 (color online). Schematic representation of the proposed orbital order pattern in the  $a$ - $b$  plane.

modulation [2,13]. This additional wave vector implies that the  $a$  and  $b$  axes of this high temperature tetragonal phase are quadrupled. However, a smaller  $A$ -centered orthorhombic unit cell, rotated by  $45^\circ$  with  $a_o \approx b_o \approx 2\sqrt{2}a_t$  and  $c_o = c_t$ , can be used to index all the reflections. The nature of this additional modulation is still unclear.  $K$  edge resonant x-ray scattering was used to claim that this quarter-wave modulation was due to orbital ordering [2]. Another study using nonresonant techniques suggested that this could be caused by cooperative Jahn-Teller distortions causing a shear-type distortion, similar to that proposed in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and  $\text{LaSr}_2\text{Mn}_2\text{O}_7$  [13]. Irrespective of the mechanism, it is clear that orbital order develops at the same temperature as the charge ordering ( $T_{\text{OO}} = T_{\text{CO}} = 240$  K).

Further cooling results in long-range spin ordering, observed by neutron scattering [10] as a complex antiferromagnetic ordering at  $T_N = 110$  K. Magnetic susceptibility measurements give a much higher antiferromagnetic transition temperature, concurrent with the charge and orbital ordering [14]. It therefore seems likely that in-plane antiferromagnetic order develops at 240 K [ $T_N(ab) = T_{\text{CO}} = T_{\text{OO}}$ ] consistent with the rodlike neutron scattering reported between  $T_N$  and  $T_{\text{CO}}$  [10]. This in-plane antiferromagnetic order then develops fully three dimensionally at  $T_N(c) = 160$  K. At the  $\text{Mn}^{3+}$  sites ( $3d^4$ ) the Hund's rule coupling is strong and the crystal field has a large cubic ( $O_h$ ) component. This causes a twofold degenerate configuration  $t_{2g}^3 e_g^1$ . This degeneracy

can be lifted by a Jahn-Teller distortion of the  $\text{MnO}_6$  octahedron reducing the symmetry to  $D_{4h}$  and separating the two components of the  $e_g^1$  level into  $3d_{3z^2-r^2}$  and  $3d_{x^2-y^2}$ . Goodenough [1] showed that the spin ordering is dependent upon the ordering of this orbital degree of freedom and, hence, a distinctive “herringbone” pattern of the orbitals is required to explain the observed antiferromagnetic spin structure. This orbital order pattern has a wave vector of  $(\frac{1}{4}, \frac{1}{4}, 0)$ .

There are thus at least two possible mechanisms to account for the observed orbital ordering. It could arise from spin ordering that forms at  $T_N$ . Alternatively, the orbital ordering could be a consequence of the cooperative Jahn-Teller that forms at  $T_{\text{CO}}$ . In some manganites, such as  $\text{LaMnO}_3$  [15] and  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [16], the extent of the Jahn-Teller distortions has been observed using crystallographic refinements of neutron and x-ray diffraction. The distortions vary between 7% and 12% suggesting that the Jahn-Teller mechanism may be important. However, in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  the  $\text{MnO}_6$  octahedra appear to be almost undistorted with a fractional change in the Mn-O bond length of only  $\approx 1\%$  [10]. This led to the suggestion that in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  the principal mechanism was the Goodenough spin mechanism.

In order to understand the interaction and interdependence of the charge, spin, orbital, and Jahn-Teller distortion degrees of freedom, it is vital to develop techniques that can distinguish between orbital and cooperative Jahn-Teller ordering. The  $K$  edge experiment of Murakami *et al.* is only an indirect indication of  $3d$  orbital ordering as they probe the  $4p$  states. Any sensitivity of the  $4p$  band to the splittings in the  $3d$  electron band was believed to arise from a combination of Coulomb interaction with the ordered  $3d$  electrons and Jahn-Teller distortions [4]. However, subsequent theoretical studies have shown that  $K$  edge experiments are about 100 times more sensitive to Jahn-Teller distortions. The obvious method is resonant scattering at the  $L$  edges, which directly probe the  $3d$  states.

The present experiments were conducted on station 5U1 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. A single crystal of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  was used with dimensions  $(4 \times 4 \times 1)$  mm<sup>3</sup>. The sample was cut and polished with  $[110]$  surface normal, and aligned in the two-circle diffractometer [17] with the  $[110]$  and  $[001]$  axes defining the diffraction plane. The beam line produces an energy resolution of  $\Delta E \approx 1$  eV at 640 eV. The incident photon energy was tuned to the manganese  $L_{\text{III}}$  edge (639 eV) and a search was undertaken for a superlattice reflection at  $(\frac{1}{4}, \frac{1}{4}, 0)$ . This reflection has a Bragg angle of  $\theta = 62.9^\circ$  at 640 eV and a clear peak was observed here; a scan taken parallel to the scattering vector is shown in the inset of Fig. 2. The peak was well defined with a Lorentzian squared line shape, significantly broader than the instrumental resolution.

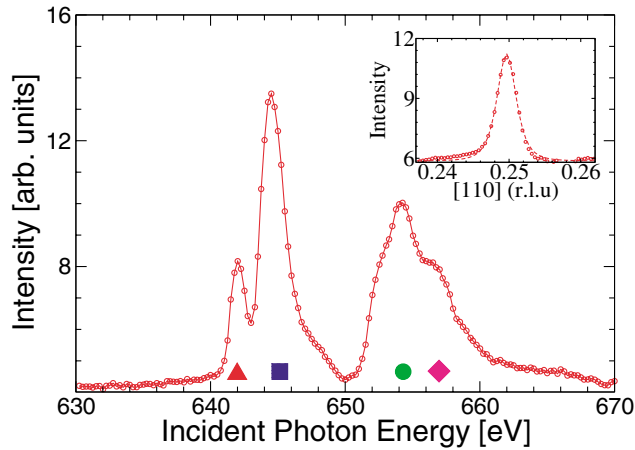


FIG. 2 (color online). Energy scan at fixed wave vector through the  $(\frac{1}{4}, \frac{1}{4}, 0)$  orbital order reflection at 140 K. The symbols ( $\blacktriangle$ ,  $\blacksquare$ ,  $\bullet$ ,  $\blacklozenge$ ) show the energies of the four major features in the scan as in Ref. [8]. The inset shows a scan taken at  $E = 641$  eV through the orbital order reflection in the  $[110]$  (longitudinal) direction. By fitting the peak to a Lorentzian squared line shape, the inverse correlation length [defined as  $\xi^{-1} = \frac{2\pi}{c}\kappa$ , where  $\kappa$  is the half width at half maximum in reciprocal lattice units (r.l.u.) and  $c$  is the direct space lattice parameter] is found to be  $2.6 \times 10^{-3} \text{ \AA}^{-1}$ .

An energy scan was then undertaken at constant wave vector, the results of which are shown in Fig. 2. No scattering above background was observed away from the  $L_{\text{III}}$  and  $L_{\text{II}}$  edges. We are therefore confident that these effects are dominated by ordering of the  $\text{Mn}^{3+}$  sublattice. The interpretation of the energy scan of Fig. 2 relies on the work of Castleton and Alterelli [8]. In their paper, they made specific predictions based on atomic multiplet calculations as to the energy dependence of the  $L$  edge orbital ordering reflection in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ . They even calculated the different types of resonance that would be observed if the orbital ordering originated from a direct Goodenough model, or as a consequence of cooperative Jahn-Teller distortions.

The energy scan of Fig. 2 displays four clear features. The calculations of Castleton and Alterelli predict four major features, which were interpreted within a simple one-electron picture of  $\text{Mn}^{3+}$ . The energy dependence carries specific information regarding the type and origin of the orbital ordering. In the  $K$  edge experiments of Murakami [2] it was impossible to differentiate between the  $3d_{3x^2-r^2}/3d_{3y^2-r^2}$  ordering and the alternative  $3d_{x^2-z^2}/3d_{z^2-y^2}$  ordering. However, Castleton and Alterelli [8] include in their paper calculations for both types of orderings that are very different. A brief comparison of our data and their calculations would suggest that the orbital ordering in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$  consists of the latter type. However, at this stage some degree of caution is required, as the calculations are not derived from experimental spectra. Further work is therefore required involving detailed fitting to the data before a definitive

answer can be given. Our work, however, does indicate, even at this early stage, the additional information available from direct measurements at the  $L_{\text{III}}$  and  $L_{\text{II}}$  edges.

The energy scan of Fig. 2 gives definitive answers as to the mechanism of the orbital ordering. As discussed earlier, the observed scattering could be due to direct Goodenough orbital ordering alone, or could be a consequence of strong cooperative Jahn-Teller distortions on the  $\text{Mn}^{3+}$  ions which causes the orbital ordering. Again, Castleton and Alterelli [8] produced detailed predictions as to the energy spectra that would be observed for each limiting case, and even for a mixture of both via a scaling parameter,  $\delta$ .  $\delta = 0$  effectively turns off the lattice distortion and simulates the effect of pure orbital ordering and no Jahn-Teller distortions. The predicted energy dependence for  $\delta = 0.005$  is given in Fig. 3(a). For such a case, and even for the case of the Jahn-Teller distortion being relatively small ( $0 < \delta < 0.25$ ), the predominant intensities should be contained in the higher energy features associated with the  $L_{\text{II}}$  edge. For a mixture of orbital ordering and Jahn-Teller distortions ( $0.25 < \delta < 0.75$ ), the intensity of the  $L_{\text{II}}$  peaks is relatively constant but there is a rapid rise in the intensity of a peak at  $\sim 642$  eV just above the  $L_{\text{III}}$  edge. Finally, for dominant Jahn-Teller distortions ( $0.75 < \delta < 1$ ) the spectral weight resides in two features close to the  $L_{\text{III}}$  edge [see Fig. 3(b)]. Our observations could not be clearer. Even in  $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ , the archetypal material for orbital ordering in which it had been claimed that Jahn-Teller distortions might be relatively small, Fig. 2 shows that cooperative Jahn-Teller distortions are the dominant

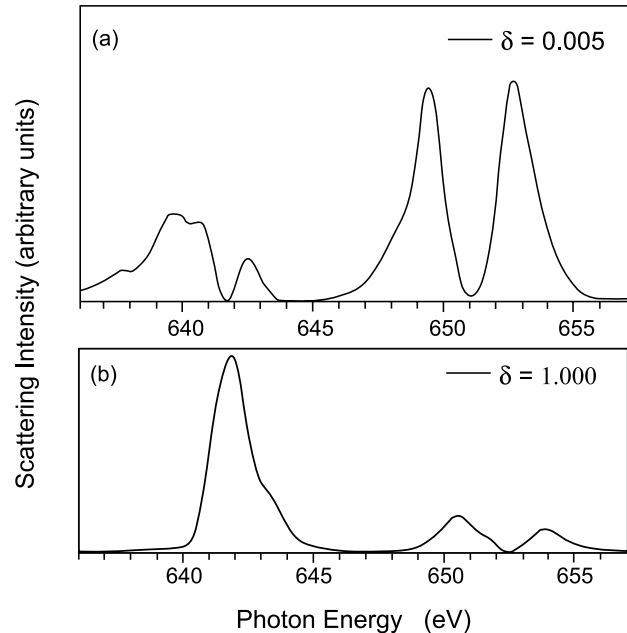


FIG. 3. Energy spectra prediction by Castleton and Alterelli [8] for the  $(\frac{1}{4}, \frac{1}{4}, 0)$  reflection with  $\delta = 0.005$  (no Jahn-Teller) and  $\delta = 1$  (strong Jahn-Teller).

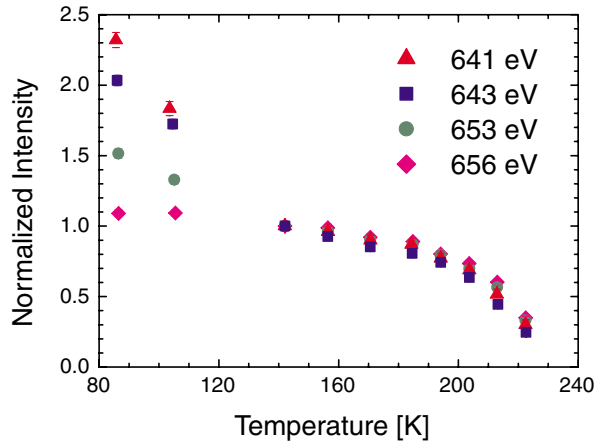


FIG. 4 (color online). Temperature dependence of the integrated intensity (measured in the longitudinal direction) of the  $(\frac{1}{4}, \frac{1}{4}, 0)$  superlattice reflection as a function of temperature of the four features in the energy spectrum. The intensities have been normalized at 140 K.

cause of the observed orbital ordering. This is simply because of the strong intensity at the  $L_{III}$  edge of the two low-energy features. However, it is also apparent that there is considerable intensity at the  $L_{II}$  edge which can be caused only by direct Goodenough orbital ordering. We therefore conclude that there are two separate contributions to the observed orbital ordering: direct Goodenough orbital ordering and strong cooperative Jahn-Teller distortions of the  $Mn^{3+}$  ions. All previous studies have considered only a single contribution to the orbital order.

The temperature dependence of the orbital ordering below the phase transition was also measured. Energy scans at constant wave vector were also taken of the orbital ordering peak to determine if the cause of such orbital ordering had a temperature dependence. A graph of the integrated intensity of the four individual energy resonances comprising the orbital order peak is shown in Fig. 4. This shows the disappearance of the orbital ordering peak as the sample is warmed up to and through the orbital ordering phase transition. Figure 4 shows that the lower energy peaks attributed to the cooperative Jahn-Teller effect become even more dominant at lower temperatures. This demonstrates that the two causes of the orbital ordering are separate, because they have a different temperature dependence. Detailed fitting of the temperature dependence will be undertaken in a future paper, but at this stage we will simply note the differing response to temperature of direct Goodenough orbital order (the features at 653 and 656 eV) and those of Jahn-Teller distortions (those at 641 and 643 eV).

In conclusion, our results demonstrate the first use of soft x-ray diffraction to probe orbital ordering. Resonant scattering at the  $L$  edge of manganese provides a direct

probe of the orbital order and provides information on the electronic configuration and the underlying mechanism of the orbital order. In  $La_{0.5}Sr_{1.5}MnO_4$ , we find that the orbital order develops at the first-order structural transition at 240 K. Jahn-Teller distortions of the  $Mn^{3+}$  ions cause considerable distortion of the  $MnO_6$  octahedra and the individual Mn-O bond lengths and angles. This, simultaneously, causes cooperative displacements of the  $Mn^{4+}$  ions and orbital ordering on the  $Mn^{3+}$  sublattice. It is likely that the strong cooperative Jahn-Teller distortions are one of the causes of orbital ordering in *all* the manganites. Finally, our results show that soft x-ray resonant diffraction will become a major technique for the study of charge, spin, and orbital ordering in a wide range of materials.

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